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(54) Title: TRIGLYCERIDE DRYING OIL AND ALKYD RESIN DERIVATIVES			
(57) Abstract Triglyceride drying oils and alkyd resins are rendered soluble or dispersible in water by reacting them with ethylene oxide in the presence of a coreactant polyol to form the drying oil derivatives, which are especially useful in various coating compositions and in agrochemical and soil-stabilisation applications.			

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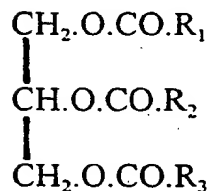
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TRIGLYCERIDE DRYING OIL AND ALKYD RESIN DERIVATIVES

This invention relates to certain triglyceride drying oil and alkyd resin derivatives, to a method of making them, and to their use in surface coatings, agrochemicals and other industries.

A triglyceride drying oil can be defined as a glycerol triester of one or more fatty acids in which the fatty acid moieties possess a sufficient level of unsaturation to enable the triglyceride oil to polymerise by thermal and oxidative means to give a solid or semi-solid polymeric structure. Such triglyceride drying oils are very useful raw materials for the surface coatings and allied industries.

Triglycerides can be represented by the formula:



where R_1 , R_2 and R_3 , which may be the same or different, are each a straight or branched chain having from 6 to 24 carbon atoms. The chains may be saturated or may contain one or more double bonds which may be conjugated or non-conjugated and can exist in either the cis or trans configuration.

The level of chain unsaturation is an important factor in determining

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the film-forming ability of triglyceride drying oils. The drying capability of an oil can be classified according to its iodine value, as follows:

Non-drying - Iodine Value less than 115

e.g. cottonseed, coconut, rapeseed, castor oils

Semi-drying - Iodine Value 115 to 150

e.g. safflower, sunflower, soybean oils

Drying - Iodine Value greater than 150

e.g. linseed, tung oils

For the purposes of the present invention, a triglyceride drying oil may be defined as an oil having the formula shown above and having an iodine value greater than 115. Examples include those given above and linola and fish oils.

Traditional decorative and protective surface coatings have been based on drying oils in their own right. Commonly used drying oils are linseed oil, tung oil and fish oil. In its simplest form, therefore, the coating formulation would comprise the drying oil, a pigment and other additives (e.g. transition metal driers) dissolved in an organic solvent. The dried film which forms following application of the coatings formulation to a substrate, results from oxidative polymerisation. This is thought to be due to the action of oxygen on the centres of unsaturation in the fatty acid chains, and is further facilitated by the presence of the fatty acids as triglycerides, wherein three fatty acid chains are already combined through an ester linkage with glycerol.

For many surface coating applications nowadays, these traditional coatings have been largely replaced by coatings based on alkyd resins which generally give better protection, last longer, dry faster and do not yellow as much

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on ageing. Alkyd resins may be thought of as polyesters that contain in their structure the functionality of unsaturated vegetable oils. They are made by esterifying triglycerides (or fatty acids) and various monofunctional and difunctional acids or anhydrides with a variety of di-, tri- and tetra-functional polyols. Thus, in its simplest form, an alkyd resin may be obtained by reaction of a triglyceride drying oil as defined above with glycerol to give a transesterified intermediate, which is further reacted with a polyfunctional acid to give the alkyd polymer, the chain length of which is determined by the ratio of mono to diglycerides in the mixture or the presence of other monofunctional species such as benzoic acid. The polyfunctional acid typically used in this reaction is phthalic anhydride and its isomers, but other acids and combinations can also be used. Alkyds can be tailored to meet many end use requirements, either by changing reactants or reactant ratios, or by including modifiers. As a consequence of this synthetic flexibility, there are several hundred alkyd resins commercially available.

A feature of all drying oil triglycerides and the traditional alkyd resins used in surface coatings is that they are insoluble in water. Organic solvents are therefore necessary to dissolve the film-forming resin, to enable the coatings composition to be applied to the substrate and facilitate film formation. Consequently, the coatings industry is a significant user of organic solvents, over half of which are hydrocarbons such as white spirit and xylol, the remainder being ketones, alcohols, glycols, glycol ethers, esters, nitroparaffins and small amounts of other materials.

It would be most advantageous to eliminate the use of organic solvents from coating formulations, primarily for environmental and economic considerations. A way of achieving this would be to use water in place of the organic solvents currently employed. However, this demands that the film-forming resins are water-soluble or water-dispersible.

Alkyd resins can be rendered water-soluble by, for example, introducing pendant carboxylic acid groups along the polymer backbone, and these

groups can then be neutralised with basic compounds to produce water-soluble soaps of the alkyd polymer. Another approach is to incorporate suitable acrylic groups into the alkyd backbone to give the so-called acrylic modified water-soluble alkyds. A disadvantage of these approaches is that they both involve relatively sophisticated synthetic organic chemistry, which detracts somewhat from the "natural" image of alkyd coatings. A further disadvantage of this acid/base route is the frequent need for substantial amounts of organic solvents such as butyl glycol or methoxy propanol in order to maintain stability and dilution characteristics.

We have now devised a method of rendering triglyceride drying oils and alkyd resins water-soluble or water-dispersible, which method reduces or overcomes the above-mentioned disadvantages. The triglyceride drying oils modified in accordance with the present invention can subsequently be used to synthesize water-soluble or water-dispersible alkyd resins.

According to one preferred aspect of the present invention, there is provided a method of making a derivative of a triglyceride drying oil or of an alkyd resin, which derivative is water-soluble or water-dispersible, which method comprises reacting the drying oil or the alkyd resin with ethylene oxide in the presence of a coreactant polyol.

The present invention also provides water-soluble or water-dispersible drying oils or alkyd resin derivatives made by the above method. The drying oil derivatives can retain much of the ability of the unmodified triglyceride to produce a dried film from oxidative polymerisation.

The invention also provides a water-soluble or water-dispersible derivative of a triglyceride drying oil, or of an alkyd resin, which is an adduct of the drying oil or alkyd resin and ethylene oxide. Preferably, the adduct contains from 20% to 90% by weight of ethylene oxide, and most preferably from 25% to 80% by weight. The adduct may be defined as a polyethoxylated partial ester derivative of a triglyceride drying oil, or a polyethoxylated derivative of an alkyd resin.

The invention further provides a water-soluble or water-dispersible alkyd resin which has been made from a water-soluble or water-dispersible triglyceride drying oil derivative of the invention. Such resins are included hereinafter in the expression "alkyd resin derivative" of the invention where the context so permits.

The triglyceride drying oils are preferably, but not necessarily, of vegetable or animal origin, that is they may be obtained directly from plants or animals, or they may be derivatives thereof. For example, castor oil is classed as a non-drying oil but can be dehydrated to introduce a further carbon-carbon double bond which can be in conjugation with the carbon-carbon double bond already present, thus forming a drying, or semi-drying oil. Dehydrated castor oil is one of the preferred oils of this invention for use in the present invention. The oils are used preferably as refined oils, but can be used in their crude form, as extracted from the plant or animal. In a further embodiment of the invention, the oils may be oxidatively or thermally polymerised prior to derivatisation.

It will be understood that the degree of water solubility and drying time of the derivatives of the invention will be influenced by the amount of ethylene oxide incorporated into the molecule. In general, the greater the amount of ethylene oxide, the greater is the water-solubility, but the drying capacity of the derivative will usually be reduced the greater the amount of ethylene oxide. Thus, the level of ethylene oxide addition can be varied to achieve an optimum balance of water solubility and drying time for a particular application. We prefer the drying oil derivatives of the invention to have an iodine value of between about 40 and 130.

Preferably, the drying oil and alkyd resin derivatives of the invention contain from 20% to 90% by weight of ethylene oxide, and most preferably from 25% to 80% by weight.

We prefer that the alkyd resin derivatives of the present invention be made from alkyd resins having an acid value of no more than 10mg KOH/g.

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Preferably they have an oil content of about 40 to 50%, for example, based on soya oil.

Examples of polyols which are suitable as coreactants are glycerol, pentaerythritol, ethylene glycol, polyethylene glycol, polyglycerol (formed by self-condensation of the glycerol unit) and trimethylol propane, although other polyols may also be used.

The polyol coreactant preferably comprises 1% to 10% by weight of the reaction mixture, and most preferably 2% to 8% by weight.

A catalyst may also be present. Preferably, an alkaline catalyst is present in the reaction mixture. Suitable catalysts are, for example, alkali metal hydroxides (such as potassium and sodium hydroxide) and alkali metal alcoholates (such as potassium ethoxide and sodium methoxide), although other catalyst systems may also be used. Suitably, the amount of catalyst present is from about 0.05% to 1% by weight of the total reaction mixture.

Thus, in accordance with a preferred embodiment of the present invention, the triglyceride drying oil or alkyd resin is reacted with ethylene oxide in the presence of 1% to 10% of a coreactant polyol, such that the final product contains from 20% to 90% ethylene oxide.

According to a further aspect of the present invention, there is provided the use of the water-soluble or water-dispersible triglyceride drying oil derivatives or alkyd resin derivatives of the invention in surface coatings and the like.

The water-soluble or water-dispersible drying oil derivatives and the alkyd resin derivatives of the invention can be used as surface coatings in their own right. The modified triglyceride drying oils may, of course, be further reacted to produce water-soluble or water-dispersible alkyd resins and these can be used, for example, in paints, inks and other surface coating compositions.

The invention thus includes an aqueous coating composition which comprises a water-soluble or water-dispersible triglyceride drying oil derivative or

alkyd resin derivative of the invention and an aqueous medium.

The invention further provides a coating composition which comprises a triglyceride drying oil derivative of the invention as such or as a part of a polymeric film-forming material.

Examples of these surface coatings compositions include undercoats for wood, architectural enamels, decorative paints, exterior wood stains, primers, topcoats for agricultural, heavy duty or general purpose applications, chassis coatings, coatings for vehicles, and coatings for railway rolling stock.

Furthermore by a suitable choice of ingredients, the compositions can be used in so-called stoving finishes or two-pack or acid catalysed or ultra-violet light-cured systems, for example. Furthermore by a suitable choice of the alkyd ingredients, the compositions can be used in so-called urethane alkyds or other modified alkyd materials, examples being chain-stopped alkyds, or acrylated alkyds, or styrenated alkyds, or resin or phenolic modified alkyds, or vinyl toluene modified alkyds, or epoxy modified alkyds, or silicone modified alkyds.

The invention may also find application by chemical or mechanical combination with the above mentioned systems or by combination with other resin systems for the coatings industry, examples being polyester and acrylic resin types of suitable compatibility.

The invention also provides for the use of the water-soluble or water-dispersible triglyceride or alkyd resin derivatives of the invention as surface coatings in agrochemical applications.

The derivatives may be utilised as adjuvants to confer rainfastness properties on all types of foliage-applied agrochemicals, such as pesticides, plant growth regulators, and others. This could be achieved by mixing the derivatives with the diluted aqueous formulation of the pesticide, that is, using the derivatives as "tank-mix" additives. Alternatively, the derivatives could be formulated directly with the pesticide as "within-formulation" additives prior to dilution for spraying. Wash-off of the active ingredients and formulation components in the spray

deposit will be reduced due to the hydrophobic character and inherent robustness of the films.

The derivatives may be used to confer anti-transparent properties to foliage-applied sprays. The derivatives may be used as tank-mix, or as within-formulation additives. This application will be especially useful for plants that are to be transplanted, or to those that have been recently transplanted, and to plants that are suffering from temporary water shortage.

The derivatives may be used to confer anti-evaporant properties to soil- or foliage-acting volatile ingredients, such as pesticides. The films thus formed will prevent excessive loss of the volatile components.

The derivatives may be used to coat the surfaces of fertilizer pellets or granules to limit the ingress of water. The derivatives may be applied undiluted directly to the pellets or granules, or may be applied after dilution in a suitable solvent.

Accordingly, in another aspect the invention provides a fertilizer composition comprising a core containing a material active as a fertilizer, and a coating of a water-soluble or water-dispersible triglyceride drying oil or alkyd resin derivative of the invention, encapsulating the core.

The term "fertilizer" refers to any plant nutrient including single-component or multi-component macro- and micronutrients. Coating with the film-forming derivatives will prolong the physical form of the pellet or granule both before and after it has been applied to the soil. Another important advantage is that there is better control over the rate of leaching of the nutrients. This has significant benefits with respect to regulating the release of the nutrients to coincide with the time of greatest demand by the crop, rather than at any time after application should rainfall occur. More efficient use of such fertilizers will limit the amount available to leach into groundwater supplies and has important environmental benefits, especially with regard to nitrate and to phosphate fertilizers.

The invention thus includes an agrochemical composition which comprises an agrochemical agent, and a water-soluble or water-dispersible triglyceride drying oil derivative or alkyd resin derivative of the invention.

The derivatives of the invention may be used to delay the ingress of water to seeds. The derivatives may be applied directly to the seeds or may be applied after dilution in a suitable solvent. This is particularly useful during conditions of water-logging when there is excessive soil water preventing the normal germination or growth of the seed. The derivatives may be applied directly to the seed, or after pelleting the seed with pesticides, pigments etc, which is a common practice for many types of crop seed.

The derivatives may be used as binders for seed coatings containing pesticides, growth regulators, pigments, etc. The film-forming properties of the derivatives will be especially useful in binding the coating ingredients to the seed as well as in preventing the coating being removed prematurely by soil water or abrasion with soil particles or by leaking by rain.

The derivatives may be used to prevent the ingress of water into fruits such as cherries at a time when water absorption would lead to fruit cracking thus damaging the fruit.

The derivatives may be used to bind soil particles together thus preventing erosion due to wind and rain. The derivatives can be applied directly to the soil, or can be applied after dilution in a suitable solvent. The film-forming properties of the derivatives have been found to be useful in binding the soil particles together.

In order that the invention may be more fully understood, embodiments thereof will now be described, by way of example only.

Example 1

Linseed oil (26% by weight), glycerol (4.0% by weight) and ethylene oxide (70% by weight) were reacted together in a 5 litre capacity reactor at a temperature of 150°C and a pressure of 2 to 3 bar in the presence of 50%

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potassium hydroxide as catalyst (0.2% by weight of total charge). Residual catalyst in the product was neutralised with lactic acid.

The ethoxylated product was totally soluble when added to distilled water at 20% and 40% by weight.

A 25 micrometre film cast from the product on a glass plate using a draw-bar produced a semi-dry, tacky film after 7 days at ambient temperature.

Example 2

Linseed oil (36.2% by weight), glycerol (3.8% by weight) and ethylene oxide (60% by weight) were reacted together using the procedure described in Example 1.

The ethoxylated product was totally soluble in water at 20% by weight.

A 25 micrometre film cast from the product on a glass plate using a draw-bar produced a slightly tacky film after 14 days at ambient temperature.

Example 3

Linseed oil (45.2% by weight), glycerol (4.8% by weight) and ethylene oxide (50% by weight) were reacted together using the procedure described in Example 1.

The ethoxylated product formed a stable dispersion when added to distilled water at 20% by weight.

A 25 micrometre film cast from the product on a glass plate using a draw-bar produced a waxy, very slightly tacky film after 7 days at ambient temperature.

Example 4

Tung oil (36.2% by weight), glycerol (3.8% by weight) and ethylene oxide (60% by weight) were reacted together in a 600ml capacity reactor at a temperature of 150°C and a pressure of 2 to 3 bar, using 50% potassium hydroxide as catalyst (0.2% by weight of total reactants). Residual catalyst in the product was neutralised with lactic acid.

The ethoxylated product was totally soluble in distilled water at 20% by weight.

A 25 micrometre film cast from the product on to a glass plate using a draw-bar produced a dry waxy film in less than 24 hours at ambient temperature.

Example 5

Tung oil (45.3% by weight), glycerol (4.6% by weight) and ethylene oxide (50% by weight) were reacted together using the procedure described in Example 4.

The ethoxylated product produced a stable emulsion when added to water at 20% by weight.

A 25 micrometre film cast on to a glass plate produced a dry waxy film within 12 hours at ambient temperature.

Example 6

Linseed oil (36.2% by weight), monoethylene glycol (3.8% by weight) and ethylene oxide (60.0% by weight) were reacted together in a 600ml capacity reactor at a temperature of 150°C and a pressure of 3 to 4 bar, using 50% potassium hydroxide as catalyst (0.2% by weight of total reactants). Residual catalyst in the product was neutralised with lactic acid.

The ethoxylated product was a clear amber liquid with an iodine value of 57 and was totally soluble in distilled water at a concentration of 50% by weight.

A 25 micrometre film cast from the product on to a glass plate using a draw-bar dried to a tacky film within seven days.

Example 7

Crude fish oil (56.0% by weight), glycerol (4.0% by weight) and ethylene oxide (40.0% by weight) were reacted together using the procedure described in Example 1 to form an ethoxylated product with similar properties.

Example 8

Sunflower oil (60.7% by weight), glycerol (6.3% by weight) and ethylene oxide (33.0% by weight) were reacted together using the procedure described in Example 1, to form an ethoxylated product with similar properties.

Example 9

Dehydrated castor oil (36.2% by weight), glycerol (3.8% by weight) and ethylene oxide (60.0% by weight) were reacted together using the procedure described in Example 1, to form an ethoxylated product with similar properties.

Example 10

Refined safflower oil (26.0% by weight), glycerol (4.0% by weight) and ethylene oxide (70.0% by weight) were reacted together using the procedure described in Example 1, to form an ethoxylated product with similar properties.

Example 11

Dehydrated castor oil (57.0% by weight), glycerol (3.0% by weight) and ethylene oxide (40.0% by weight) were reacted together using the procedure described in Example 1, to form an ethoxylated product with similar properties.

Example 12

Crude fish oil (76.0% by weight), glycerol (4.0% by weight) and ethylene oxide (20.0% by weight) were reacted together using the procedure described in Example 1, to form an ethoxylated product with similar properties.

Example 13

A 60% ethoxylated linseed oil derivative of the invention (65.9% by weight) was reacted with isophthalic acid (20.5% by weight) and trimethoylpropane (13.6% by weight) at 220°, under a nitrogen gas sweep and a toluene reflux. The reaction was stopped when the acid value of the mixture was less than 15 mgKOH/g resin.

The alkyd resin product was soluble in water at 20% and 40% by weight. A 50 micrometre film cast on a glass plate using a draw bar produced a semi-dry, tacky film after 7 days at ambient temperature.

CLAIMS:

1. A method of making a water-soluble or water-dispersible derivative of a triglyceride drying oil or of an alkyd resin, which comprises reacting the drying oil or the alkyd resin with ethylene oxide in the presence of a coreactant polyol.
2. A method according to claim 1, wherein the derivative is of a triglyceride drying oil and contains from 20% to 90% by weight of ethylene oxide, the derivative retaining the property of the drying oil to form a dried film by oxidative polymerisation.
3. A method according to claim 2, wherein the derivative has an iodine value of from 40 to 130.
4. A method according to claim 1, 2 or 3, wherein the derivative contains from 25% to 80% by weight ethylene oxide.
5. A method according to claim 1, 2, 3 or 4, wherein the coreactant polyol is glycerol, pentaerythritol, ethylene glycol, polyethylene glycol, polyglycerol or trimethylol propane.
6. A method according to claim 5, wherein the coreactant polyol comprises from 1% to 10% by weight of the reaction mixture of drying oil or alkyd resin, ethylene oxide and coreactant polyol.
7. A method according to claim 6, wherein the coreactant polyol comprises from 2% to 8% by weight of said reaction mixture.

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8. A method according to any preceding claim, wherein the reaction is effected in the presence of a catalyst.
9. A method according to claim 8, wherein the catalyst is alkaline.
10. A method according to claim 1, wherein the derivative is of an alkyd resin and wherein the alkyd resin has an acid value of at most 10 mg KOH/g.
11. A method according to claim 10, wherein alkyd resin has an oil content of about 40% to 50%.
12. A method of making a water-soluble or water-dispersible derivative of a triglyceride drying oil or of an alkyd resin, substantially as herein described in any of Examples 1 to 12.
13. A water-soluble or water-dispersible derivative of a triglyceride drying oil or of an alkyd resin, when made by the method of any of claims 1 to 12.
14. A water-soluble or water-dispersible derivative of a triglyceride drying oil which is an adduct of the drying oil and ethylene oxide.
15. A derivative according to claim 14, which has an iodine value of from 40 to 130.
16. A water-soluble or water-dispersible derivative of an alkyd resin which is an adduct of the resin and ethylene oxide.
17. A derivative according to claim 14, 15 or 16, which contains from 20% to 90% by weight of ethylene oxide.

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18. A derivative according to claim 14, substantially as herein described in any of Examples 1 to 12.

19. A water-soluble or water-dispersible alkyd resin which has been made from a water-soluble or water-dispersible triglyceride drying oil derivative as claimed in claim 14, 15, 17 or 18.

20. An aqueous coating composition which comprises a water-soluble or water-dispersible triglyceride drying oil derivative or alkyd resin derivative as claimed in any of claims 13 to 19, and an aqueous medium.

21. A composition according to claim 20 which is in the form of a paint, an ink or another surface coating composition.

22. An agrochemical composition which comprises an agrochemical agent, and a water-soluble or water-dispersible triglyceride drying oil derivative or alkyd resin derivative as claimed in any of claims 13 to 19.

23. A composition according to claim 22, wherein the agrochemical agent is a pesticide, plant growth regulator or fertiliser.

24. The use of a composition according to claim 20 for coating an article or plant to confer anti-transparent, anti-evaporant or anti-water-ingress properties thereto.

25. The use according to claim 24, wherein the article is a seed or fertiliser pellets or granules.

26. The use of a composition according to claim 20 for application to

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soil to bind the soil particles together.

INTERNATIONAL SEARCH REPORT

Inter- national Application No
PCT/GB 96/02215

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08G63/48 C11C3/00				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08G C11C				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	DE 694 178 A (I. G. FARBENINDUSTRIE AG) 27 June 1940 see the whole document	1-9, 12-15, 17,18, 20,21		
X	GB 1 099 777 A (LEDOGA SPA) 17 January 1968 see claims 1-21	1-9, 12-15, 17,18, 20,21		
X	US 4 681 900 A (IWASAKI) 21 July 1987 see claims 1-10	1-9, 12-15, 17,18, 20,22-26		
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Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">19 December 1996</div>	Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">06.01.97</div>			
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer <div style="text-align: center; font-weight: bold;">Decocker, L</div>			

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